

# Density Functional Studies of Cation–Water Complexes

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**ABSTRACT:** By using density functional *ab initio* techniques the equilibrium structure, binding energy, and electronic distribution were determined for  $[X(H_2O)_n]^{+k}$ . Specifically, when  $X = H, Li$ , and  $Na$ ,  $k = +1$  and when  $k = +2$ ,  $X = Be$  and  $Mg$ . In all cases the number of water molecules varies from one through four. A correlation between the distribution of the positive charge and the binding energy of the complex was encountered. A connection between simple arguments used to describe solvation in the bulk and the results obtained here for clusters was established. © 2000 John Wiley & Sons, Inc. *J Comput Chem* 21: 63–68, 2000

**Keywords:** density functional; hydrated cations; solvation; clusters

## Introduction

The notion of solvation in the bulk is often explained in terms of simplistic models<sup>1</sup> where the so-called solvation number is used as a parameter that intends to measure how solvated a species is. Usually, simple concepts of packing are used to determine this parameter. For example, the extent to which an ion is hydrated is determined by the number of water molecules around the ion with properties that can be distinguished from water in the bulk. Additionally, these approaches use concepts related to the stabilization of the solvated species by the formation of mix clusters, which are  $X(H_2O)_n$

clusters where  $X$  can be any atom or molecule. These models do not provide any explanation of possible electronic rearrangement within the cluster, which might be considerable and important in the stabilization of the system. A good example of this is the study of the solvated proton where various solvation numbers have been proposed.<sup>2</sup> These systems,  $[H(H_2O)_n]^+$ , have been recently studied<sup>3,4</sup> using *ab initio* theoretical techniques similar to the ones used in the present investigation. The results of this study suggest that for certain size clusters the possible identification of the solvated proton is mainly difficult because of considerable distortion in the electronic environment. This phenomenon has been previously explained in terms of the migration of the proton in water, which is associated with the rearrangement of covalent and hydrogen bonds.

The interaction of different cations solvated in water was studied using electronic structure calcu-

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lations. Specifically, Glendening and Feller<sup>5</sup> studied the structure and energy of  $M^+(H_2O)_n$  clusters for  $M = Li, Na, K, Rb,$  and  $Cs$  using Hartree–Fock and post-Hartree–Fock techniques. They found that small clusters favor structures in which each water molecule is bound to the cationic species, whereas larger clusters show equilibrium structures that suggest the formation of a secondary solvation shell. Feller and coworkers<sup>6</sup> found similar results for  $Li^+(H_2O)_n$  ( $n = 1–6$ ) using larger basis sets. Bauschlicher et al.<sup>7</sup> also found that the lowest energy equilibrium structure for a sodium atom solvated by up to four water molecules resembles a single solvation shell. On the other hand, Pavlov et al.<sup>8</sup> used density functional theory to consider doubly charged hydrated cations. Specifically, the geometry and energy of hydrated beryllium, magnesium, calcium, and zinc were computed and explained in terms of electrostatic arguments. For example, the smaller cations tend to have larger binding energies because of the strong electrostatic attraction when compared to the larger cations. Also, the coordination number for each of the cations was presented and compared with experimental values.

In the present study we considered the electronic structure of various positively charge mixed clusters. Specifically, five different cations,  $H^+, Li^+, Na^+, Be^{+2},$  and  $Mg^{+2}$  hydrated by various water molecules, which are  $[X(H_2O)_n]^{+k}$ , were studied using the density functional formalism. A relation between the supermolecule binding energy, the charge delocalization, and simple solvation models was established for these systems.

## Theoretical Model

The theoretical model used in this study is based on *ab initio* techniques within the density functional approximation. Specifically, the nonlocal Becke exchange<sup>9</sup> was used coupled with the Lee–Yang–Parr gradient-corrected correlation energy functional<sup>10,11</sup> (BLYP). A contracted Gaussian-type split valence basis set including both polarization and diffuse functions (i.e., 6-31+G\*\*<sup>12</sup>) was used for all calculations discussed here. For all the systems studied a full geometry optimization was performed and various initial geometries in the optimization procedure were used to guarantee the determination of the lowest energy equilibrium structure. All calculations were performed using the Gaussian 92-DFT software program<sup>13</sup> installed on a SUN Ultra 2 Workstation.

The Mulliken population analysis<sup>14</sup> was used to characterize the charge distribution of the cationic

systems considered here. In particular, the distribution of the positive charge was computed for both the solvated species and the molecular components of the cluster. For example, for  $[Li(H_2O)_2]^+$  the distribution of the positive charge was computed for the Li atom and for the two  $H_2O$  molecules. The charge distribution of the water molecules was computed by adding the atomic population of the components.

In order to probe the convergence of the charge distribution with variations in the basis set, preliminary calculations were performed for some of the systems. It was observed that for the 3-21G\* basis set the charge density computed around the cation was, in most cases, smaller than the density computed using the other two basis sets that were much larger. The difference in charge distribution between the 6-31+G\*\* and the D95+\*\* is insignificant. Hence, for computational reasons the 6-31+G\*\* basis set was chosen. Similar calculations were performed using various density functionals available in Gaussian 92-DFT and no significant changes were observed between the various methods.

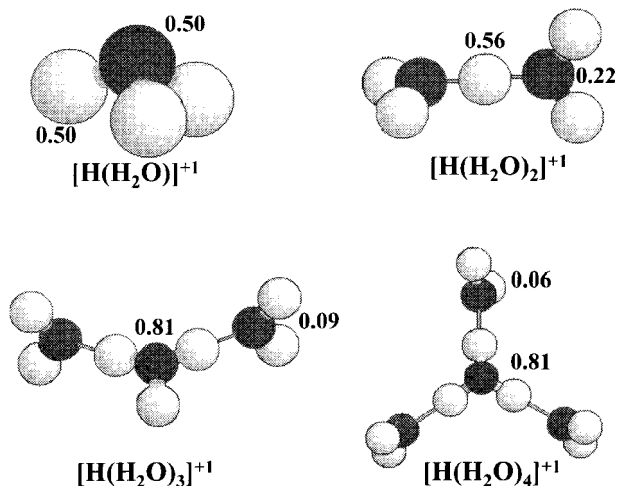
The binding energy of each complex,  $\Delta E_{[X(H_2O)_n]^{+k}}$ , was computed using the supermolecule approach,

$$\Delta E_{[X(H_2O)_n]^{+k}} = E_{[X(H_2O)_n]^{+k}} - E_{X^{+k}} - E_{(H_2O)_n}, \quad (1)$$

where  $E_M$  represents the energy of the  $M$  species. It is important to state that a full geometry optimization was performed for all the  $[X(H_2O)_n]^{+k}$  systems and the corresponding pure water cluster. In terms of energetic arguments, it is expected that as the binding energy gets larger the energy of solvation for the cationic species increases and hence the cation is more solvated. Also, preliminary calculations were performed to determine the magnitude of the basis set superposition error (BSSE) for these systems using the counterpoise correction.<sup>15</sup> In all cases, the magnitude of the BSSE was less than 0.5 kcal/mol that, compared to the values of the binding energies obtained, was negligible.

## Results and Discussion

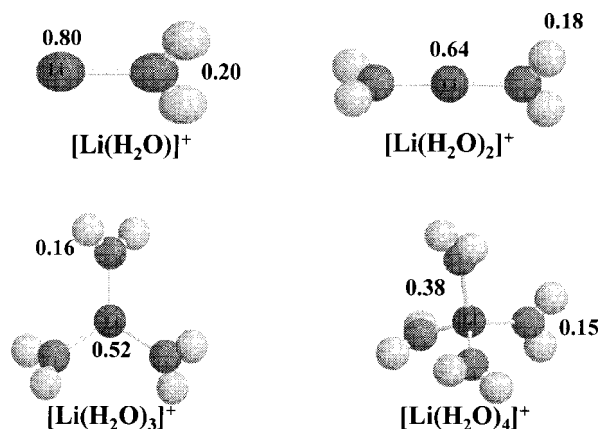
As stated, a full geometry optimization for the  $[H(H_2O)_n]^+, [Li(H_2O)_n]^+, [Na(H_2O)_n]^+, [Be(H_2O)_n]^{+2},$  and  $[Mg(H_2O)_n]^{+2}$  clusters with  $n = 1–4$  was performed using DFT-BLYP/6-31+G\*\* technique. The structures of these systems are shown in Figures 1–5 with the Mulliken population analysis for the cation and the water molecules specified. It is important to state that the distribution of the positive charge was computed for



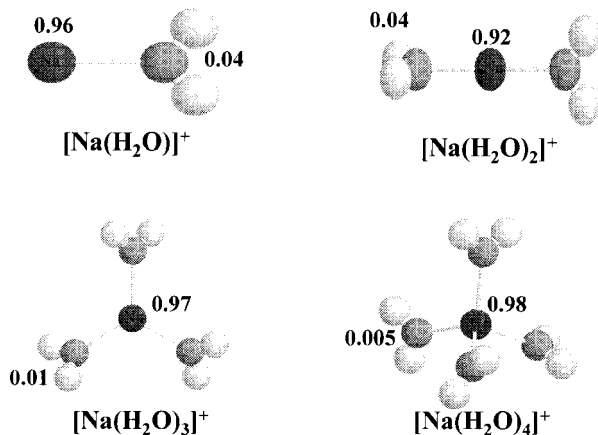
**FIGURE 1.** The lowest energy equilibrium structures for  $[\text{H}(\text{H}_2\text{O})_n]^+$  for  $n = 1-4$ . The numbers shown for each atom are the Mulliken population in all figures.

the cation and for each water molecule forming the cluster and these are shown in Table I. As mentioned in the previous section, in the case of the water molecules the charge distribution was calculated by taking into account the atomic population of the components. For example, for the  $[\text{H}(\text{H}_2\text{O})]^+$  system the water molecule contains a 0.51 net charge that is obtained by adding the atomic population corresponding to the oxygen and each hydrogen atom. For this particular system the oxygen has a charge of  $-0.43$  and each hydrogen atom has a charge of  $0.47$ .

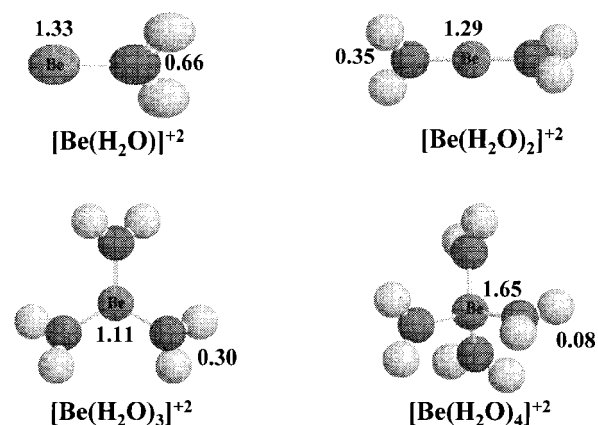
Figure 1 shows the lowest energy equilibrium structure for the  $[\text{H}(\text{H}_2\text{O})_n]^+$  complexes. It can be observed that for  $n = 1$  and  $2$  the  $\text{H}_2\text{O}$  molecule(s) are attached to the “proton” that, when the complex



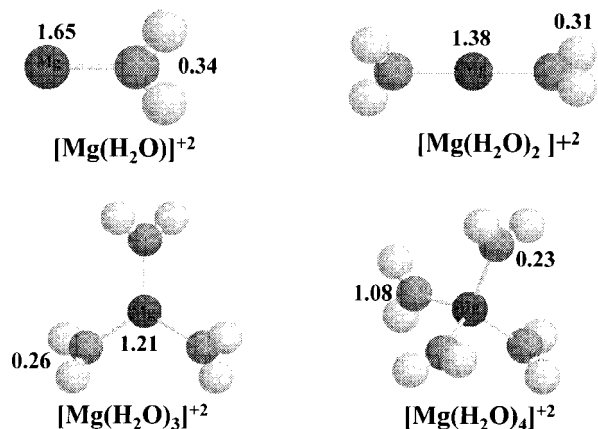
**FIGURE 2.** The lowest energy equilibrium structures for  $[\text{Li}(\text{H}_2\text{O})_n]^+$  for  $n = 1-4$ .



**FIGURE 3.** The lowest energy equilibrium structures for  $[\text{Na}(\text{H}_2\text{O})_n]^+$  for  $n = 1-4$ .



**FIGURE 4.** The lowest energy equilibrium structures for  $[\text{Be}(\text{H}_2\text{O})_n]^{+2}$  for  $n = 1-4$ .



**FIGURE 5.** The lowest energy equilibrium structures for  $[\text{Mg}(\text{H}_2\text{O})_n]^{+2}$  for  $n = 1-4$ .

is formed, has a net charge of 0.49 or 0.56, depending on the system. The remainder of the charge is distributed among the water molecules forming the system as shown in Table I. When  $n = 1$  the system can be viewed as a hydronium molecule that is almost symmetric in its charge density. The non-equivalence of the hydrogen atoms might be due to the approximations used in this study (i.e., basis set, method, and population analysis). For  $n = 2$  the charge that is not localized on the proton is equally distributed between the two water molecules in a symmetrical way.

In the case of  $n = 3$  the solvated “proton” cannot be identified; instead the central water molecule is similar to a hydronium molecule with a net charge of 0.81. The other two molecules have a net charge of 0.09. It is important to mention that in the optimization procedure, for  $n = 3$  an initial structure with the water molecules surrounding the proton was used and the same equilibrium structure as the ones discussed was obtained. A similar structure can be observed for the  $n = 4$  cluster where the center unit resembles a hydronium molecule surrounded by three water molecules. Again, the charge of the hydronium molecule equals 0.81 and all other water molecules are equivalent. These results are in good agreement with previous studies<sup>3, 4</sup> using methods similar to the ones employed here.

As in the case of pure water clusters, the formation of hydrogen bonding is evident for all clusters discussed above except  $n = 1$ . It is clear that in all these complexes the identification of the classical proton (i.e., hydrogen with a positive one charge) is not possible because the charge is not confined to the “proton,” but instead it is distributed throughout the system. The same behavior is observed when a hydronium molecule can be identified. The net charge for this molecule is 0.81, which is not the classical +1 charged system.

The lowest energy equilibrium structures for the  $[\text{Li}(\text{H}_2\text{O})_n]^+$  system are shown in Figure 2. Contrary to the results for the protonated water clusters, in all cases the Li atom is surrounded by water molecules and as the number of molecules increases the charge on the cation decreases. In all cases the charge distribution between the various water molecules within a given cluster is equal. The distance between the Li and the oxygen in the different water molecules is approximately the same, but as the number of water molecules increases this distance also increases. In the case of  $[\text{Li}(\text{H}_2\text{O})_3]^+$  another isomer was found at a higher energy that resembles the  $[\text{Li}(\text{H}_2\text{O})_2]^+$  structure but with the third water molecule attached to one water molecule. More interesting is the fact

**TABLE I.** Charge Distribution of Clusters Calculated Using Mulliken Population Analysis.

<i>n</i>	Cation	H <sub>2</sub> O
<hr/>		
[H(H <sub>2</sub> O) <sub><i>n</i></sub> ] <sup>+</sup>		
<hr/>		
1	0.49 (49%)	0.51 (51%)
2	0.56 (56%)	0.22 (44%)
3	—	0.09
4	—	0.06
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[Li(H <sub>2</sub> O) <sub><i>n</i></sub> ] <sup>+</sup>		
<hr/>		
1	0.80 (80%)	0.20 (20%)
2	0.64 (64%)	0.18 (36%)
3	0.52 (52%)	0.16 (48%)
4	0.38 (38%)	0.15 (60%)
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[Na(H <sub>2</sub> O) <sub><i>n</i></sub> ] <sup>+</sup>		
<hr/>		
1	0.97 (97%)	0.03 (3%)
2	0.92 (92%)	0.04 (8%)
3	0.95 (95%)	0.01 (3%)
4	0.98 (98%)	0.01 (4%)
<hr/>		
[Be(H <sub>2</sub> O) <sub><i>n</i></sub> ] <sup>+2</sup>		
<hr/>		
1	1.33 (67%)	0.66 (33%)
2	1.29 (65%)	0.35 (35%)
3	1.11 (56%)	0.30 (45%)
4	1.65 (83%)	0.08 (16%)
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[Mg(H <sub>2</sub> O) <sub><i>n</i></sub> ] <sup>+2</sup>		
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1	1.65 (83%)	0.34 (17%)
2	1.38 (69%)	0.31 (31%)
3	1.21 (61%)	0.26 (39%)
4	1.08 (54%)	0.24 (48%)
<hr/>		

The charge distribution of the water molecules is computed by adding the atomic population of the components. The numbers in parentheses are the percentage of positive charge in the atom or molecule. The cation was not identified.

that no formation of hydrogen bonding is observed for all of the lithium systems but instead the water molecules are staged with respect to each other.

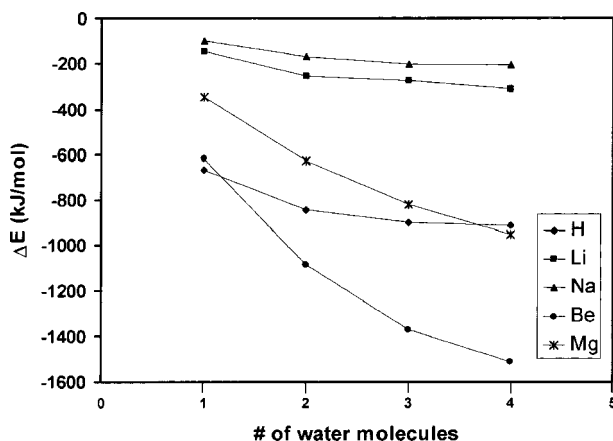
Figure 3 shows the lowest energy equilibrium structure for  $[\text{Na}(\text{H}_2\text{O})_n]^+$  clusters. The results obtained are very similar to the ones discussed for  $[\text{Li}(\text{H}_2\text{O})_n]^+$  in terms of the geometrical arrangement of molecules around the cation. As expected,

the distance between the sodium atom and the water molecules is larger than in the case of the lithium clusters because of the size of the sodium atom. However, in all cases between 92% and 98% of the positive charge is located on the Na atom. Contrary to the lithium complexes, only small variations in the charge distribution of the sodium atom are observed as the number of water molecules increases in the cluster. This is because the water molecules in the  $[\text{Na}(\text{H}_2\text{O})_n]^+$  complexes, which are located at very large distances from the cation, are not affected by the positive charge. Hence, the water molecules in these systems are not involved in the charge delocalization phenomena.

Figures 4 and 5 show the lowest energy equilibrium structure for  $[\text{Be}(\text{H}_2\text{O})_n]^{+2}$  and  $[\text{Mg}(\text{H}_2\text{O})_n]^{+2}$  clusters, respectively. In all cases the water molecules are surrounding the metallic center in a staged arrangement. As in the +1 complexes it can be seen that as the number of water molecules increases the charge distribution decreases around the central atom. Also, when systems with the same number of water molecules are compared the charge distribution is more delocalized in the Be complexes than in the Mg systems. This is similar to what was observed for the previous complexes, where for smaller nuclei the charge distribution was more delocalized. When comparing complexes having the central atom in the same period of the periodic table and the same number of water molecules (i.e., Li vs. Be and Na vs. Mg), it can be noticed from Table II that the percent charge in the central atom in the +2 complexes is smaller than in the +1 systems. In particular, the difference is more pronounced between Na and Mg. These results are in agreement with the previously mentioned study by Pavlov et al.<sup>8</sup>

As expected, as the delocalization of the positive charge increases the distortion of the water molecules in the cluster also increases. For example, in the protonated complexes the bond angle and bond lengths of the water molecule increase, but in the sodium and magnesium clusters the water molecules are very similar to isolated neutral water molecules.

Figure 6 shows the values for the binding energy for the various complexes as a function of the number of water molecules. It can be seen that for the +1 complexes the binding energy does not change much as the number of water molecules in the cluster increases. Hence, the binding energy for these complexes seems to be determined basically by the interaction between one water molecule and the cationic species. On the other hand, in the +2 complexes the binding energy decreases as the number



**FIGURE 6.** The variation in the binding energy as a function of the number of water molecules in the cluster for the systems considered here. The points are connected for visual guidance.

of water molecules increases. A possible explanation for this is that because of the +2 charge the number of water molecules that can surround the metallic center is larger than in the +1 complexes. Therefore, a larger number of water molecules will be needed to reach a convergence value in the interaction energy.

When the binding energy for the different complexes are compared, it can be observed that there is a significant difference between them. Specifically, when complexes with the same charge are compared, the proton has a binding energy larger than Li and Li is larger than Na. If the binding energy is viewed as an approximated measurement of the solvation of a species, our results imply that the proton can be solvated to a greater extent than the lithium and sodium cations. In the +2 complexes the value of the binding energy for the Be systems is approximately 2 times the values of Mg systems. On the other hand, when the binding energies between species in the same period are compared, the +2 systems have larger values than the +1 clusters. This result is in agreement with the simple idea that as the ionic radius gets smaller the process of solvation is favored. Namely, as the Pauling ionic radius of the hydrated species increases the enthalpy of hydration is smaller. Moreover, the ordering in binding energies encountered for these groups of complexes follows the same ordering that is observed for the enthalpy of solvation.<sup>15</sup>

It is interesting to note that a correlation between the delocalization of the positive charge and binding energy can be recognized. The  $[\text{H}(\text{H}_2\text{O})_n]^+$  complexes generally have a larger charge delocal-

ization followed by the  $[\text{Li}(\text{H}_2\text{O})_n]^+$  and finally the  $[\text{Na}(\text{H}_2\text{O})_n]^+$  systems. From Figure 6 the same trend is observed for the binding energy. Hence, as the positive charge is more delocalized in the complexes the solvation of the cation is favored. The same behavior is observed when the complexes with +2 charge are analyzed.

## Conclusion

In the present study the equilibrium structure of various hydrated cations was considered using state of the art *ab initio* techniques. The lowest energy equilibrium structures obtained were in accord with previous theoretical studies.<sup>3-7</sup> The binding energy for each cluster was calculated and related to the delocalization of the positive charge. Based on the assumption that the solvation process is driven in part by the magnitude of the binding energy between the solvated species and the water molecules, a relation between charge delocalization and solvation was established: as the system becomes more delocalized, the solvation is stronger.

It is clear that models based on the behavior of finite systems cannot explain the process of solvation. However, basic trends related to the energy based on electronic changes can be uncovered and related to behavior observed in the bulk. More realistic models need to consider larger systems and the inclusion of temperature effects through statistical mechanical models. Work is in progress that is related to these issues.

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15. Table 9.2 of ref. 1 presents the enthalpies of solvation for various cations at 298 K.